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# Low resistance Ohmic contact to p-type crystalline silicon via nitrogen-doped copper oxide films

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This work explores the application of transparent nitrogen doped copper oxide ( $\text{CuO}_x\text{:N}$ ) films deposited by reactive sputtering to create hole-selective contacts for p-type crystalline silicon (c-Si) solar cells. It is found that  $\text{CuO}_x\text{:N}$  sputtered directly onto crystalline silicon is able to form an Ohmic contact. X-ray photoelectron spectroscopy and Raman spectroscopy measurements are used to characterise the structural and physical properties of the  $\text{CuO}_x\text{:N}$  films. Both the oxygen flow rate and the substrate temperature during deposition have a significant impact on the film composition, as well as on the resulting contact resistivity. After optimization, a low contact resistivity of  $\sim 10 \text{ m}\Omega \text{ cm}^2$  has been established. This result offers significant advantages over conventional contact structures in terms of carrier transport and device fabrication. *Published by AIP Publishing.*  
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In recent years, the development of advanced contact structures to selectively transport electrons or holes has gathered increasing interest within the c-Si photovoltaic community. Since the recombination losses in the silicon bulk and non-contacted surface regions can be minimised by various techniques,<sup>1–3</sup> the losses in the metal-contacted regions have become a major challenge for c-Si solar cells. Recently, a range of metal oxides and alkali metal salts have been investigated for their potential applications as selective contacts.<sup>4–8</sup> The hole-selective contact structures typically require high work function materials. Candidates for that purpose include molybdenum oxide ( $\text{MoO}_x$ ), vanadium oxide ( $\text{VO}_x$ ), and tungsten oxide ( $\text{WO}_x$ ).<sup>9</sup> A very low contact resistivity of  $1 \text{ m}\Omega \text{ cm}^2$  has been reported for  $\text{MoO}_x$  on p-type crystalline silicon,<sup>10</sup> and efficient solar cells utilising this material have also been demonstrated.<sup>11–13</sup> At this early stage of selective-contact research, there is a compelling motivation to explore other potential candidate materials. This study demonstrates that copper oxide is able to form a hole-selective contact directly on top of a lowly doped p-type crystalline silicon substrate.

Copper oxide is particularly attractive, given the abundance, sustainability and nontoxicity of copper and oxygen. Numerous studies of its fundamental properties have been conducted. Cuprous oxide ( $\text{Cu}_2\text{O}$ ) has been used as a p-type semiconductor in thin film solar cell research.<sup>14</sup> However, there is a lack of studies on the applications of copper oxides to crystalline silicon solar cells. In general, there are two naturally stable phases of copper oxide: cuprous oxide ( $\text{Cu}_2\text{O}$ ) and cupric oxide ( $\text{CuO}$ ); while paramelaconite ( $\text{Cu}_4\text{O}_3$ ) is an unstable phase that will not be discussed in this study. Due to their different chemical compositions and physical structures,  $\text{Cu}_2\text{O}$  and  $\text{CuO}$  have significantly different electrical and optical properties.<sup>15</sup>  $\text{Cu}_2\text{O}$  can react with  $\text{O}_2$  and transform into  $\text{CuO}$  at temperatures above  $\sim 300^\circ\text{C}$  or in oxygen-rich deposition ambient.<sup>15–17</sup>  $\text{Cu}_2\text{O}$  is naturally p-type, with a bandgap of  $\sim 2.1\text{--}2.2 \text{ eV}$  and a work function of  $\sim 4.8\text{--}5.0 \text{ eV}$ .<sup>15,18,19</sup>

The origin of its p-type conductivity is a cation deficiency, which causes defects in the lattice that serve as transporting media for holes.<sup>20,21</sup> Studies in recent years have demonstrated that the  $\text{Cu}_2\text{O}$  can be extrinsically doped with various elements, such as N, Si, F, and Cl.<sup>22–26</sup> In this work, nitrogen doping is investigated. This  $p^+$  doping shifts the Fermi level towards the valence band and confers  $\text{CuO}_x\text{:N}$  ( $x < 1$ ) an improved conductivity for holes. On the other hand,  $\text{CuO}$  cannot be doped. As a result,  $\text{Cu}_2\text{O}$ , or its doped form  $\text{CuO}_x\text{:N}$ , is the preferred oxide phase for highly conductive, hole contact regions.

The copper oxide films studied in this work were deposited by reactive RF sputtering using a 5 N pure copper target. To obtain  $\text{CuO}_x\text{:N}$  films, Ar gas at a flow rate of 20 sccm was used as the main plasma source, while the  $\text{O}_2$  and  $\text{N}_2$  gases with varying flow rates were introduced as the reactive gases. The resulting sputtered  $\text{CuO}_x\text{:N}$  films consist of a mixture of various copper oxide phases, and the final composition strongly depends on the specific deposition conditions. This means that a good control of the deposition process is critical.

It has been found that the oxygen flow can affect the film properties significantly. X-ray photoelectron spectroscopy (XPS) measurements have been used to determine the atomic composition of the deposited materials. The measured data for films with varying oxygen flow rates are presented in Figure 1(a). As reported in the literature, the binding energy peak position for copper is an indicator of the specific oxide phase.<sup>27–29</sup> Figure 1(a) presents the XPS peaks in the 930–937 eV region, which stand for  $\text{Cu}2p_{3/2}$  and is commonly used to identify Cu atoms. There is a clear shift from  $\sim 932 \text{ eV}$  to  $\sim 934 \text{ eV}$ , which indicates a transition from  $\text{Cu}_2\text{O}$  to  $\text{CuO}$  when a higher  $\text{O}_2$  flow is used.<sup>17,27,30</sup> Similarly, the full-width at half-maximum (FWHM)  $\Gamma$  values, shown in Figure 1(b), also reveal the existence of  $\text{CuO}$  at an  $\text{O}_2$  flow of 2.0 sccm. A  $\Gamma$  value of 3.0 eV matches well other values reported in the literature.<sup>27,29</sup> Although not shown in Figure 1, a satellite energy peak in the vicinity of 942–944 eV, which is also characteristic of  $\text{CuO}$ , has been observed for all the films.

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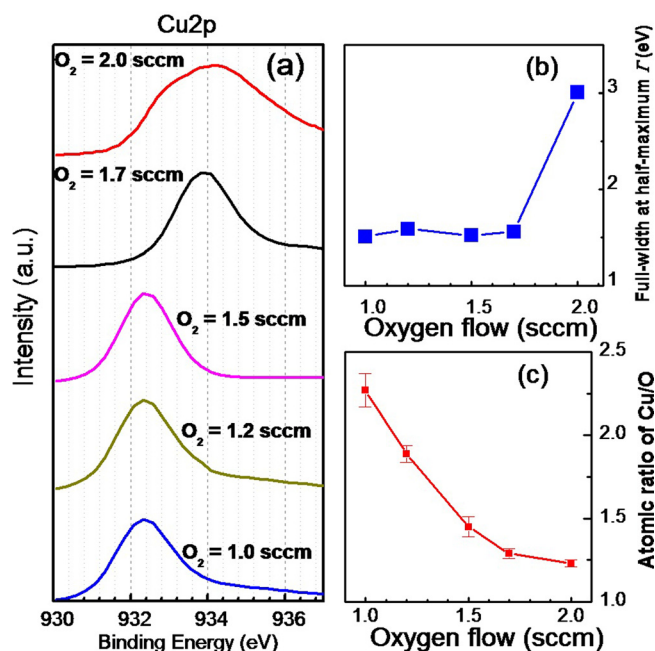


FIG. 1. X-ray photoelectron spectroscopy measurement results for  $\text{CuO}_x\text{:N}$  films deposited with different oxygen flow rates. (a) XPS result for the Cu region; (b) the fitted full width at half maximum; (c) the atomic ratio of Cu/O from surface analysis.

Figure 1(c) shows the calculated atomic ratio between copper and oxygen, considering the variations across the whole layer. As a higher oxygen concentration is used, the films become more oxygen rich, implying that more CuO is formed. An  $\text{O}_2$  flow of 1.0 sccm results in a Cu/O ratio above 2. Such a high ratio is evidence of a copper-rich material, possibly due to Cu precipitates or  $\text{CuN}_x$  formation. Most deposition conditions give a Cu/O ratio in the range between 1 and 2, which means that the sputtered films are a mixture of CuO and  $\text{Cu}_2\text{O}$ .

Another important finding from the XPS measurements is the presence of an atomic nitrogen concentration of around 0.7%–1% for samples with a high  $\text{Cu}_2\text{O}$  content, which constitutes an evidence of nitrogen doping in the film. On the other hand, films where CuO is the dominant phase ( $\text{O}_2 = 1.7$  or 2.0 sccm) show a negligible amount of nitrogen, which is consistent with the non-dopable character of CuO.

Raman spectroscopy has also been performed to characterise the material species and crystallinity of these sputtered  $\text{CuO}_x\text{:N}$  films. Numerous studies have reported the Raman behaviour of copper oxides.<sup>31–33</sup> Figure 2 shows the Raman data using a 532 nm green laser, for films deposited at different substrate temperatures and various oxygen flow rates. The top graph presents data for different oxygen flows with the substrate temperature fixed at 100 °C. The broad peak in the 500–600  $\text{cm}^{-1}$  region is a characteristic peak of  $\text{Cu}_2\text{O}$ , as reported by other studies.<sup>31–34</sup> The intensities and widths of this  $\text{Cu}_2\text{O}$  peak are closely related to the oxygen concentration. When the oxygen flow increases from 1.0 sccm to 1.5 sccm, the  $\text{Cu}_2\text{O}$  peak feature becomes broader and stronger in intensity. This change correlates with the increased  $\text{Cu}_2\text{O}$  content in the film, also confirmed by the XPS results. In contrast, higher oxygen flows result in a weaker peak in this region, which indicates that the sputtering process tends to form CuO instead of  $\text{Cu}_2\text{O}$  when there is a high oxygen

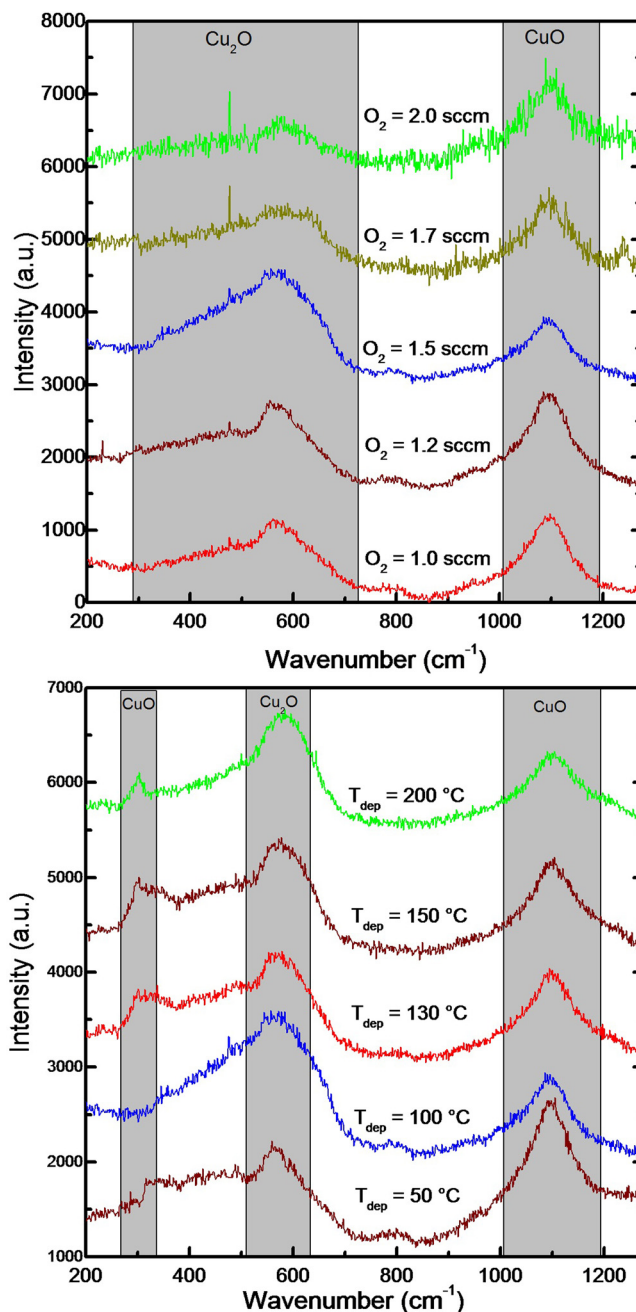


FIG. 2. Raman spectroscopy measurements for  $\text{CuO}_x\text{:N}$  films sputtered under various conditions. Top graph: fixed power of 100 W, substrate temperature of 100 °C, thickness of 8 nm, pressure of 4 mTorr; various oxygen flow rates from 1.0 to 2.0 sccm. Bottom graph: fixed power of 100 W, oxygen flow of 1.5 sccm, thickness of 8 nm, pressure of 4 mTorr; various substrate temperatures from 50 °C to 200 °C.

concentration in the plasma. The broad and relatively strong feature near 1100  $\text{cm}^{-1}$  is the indicator of the CuO phase.<sup>31,35</sup> This feature is observable in all the samples, indicating that the formation of a certain amount of CuO is unavoidable. Hence, these Raman measurements confirm the conclusions from XPS analysis that sputtered  $\text{CuO}_x\text{:N}$  films are a mixture of CuO and  $\text{Cu}_2\text{O}$ .

The bottom graph of Figure 2 presents the Raman spectra for films deposited in the temperature range of 50–200 °C, with the oxygen flow rate kept constant at 1.5 sccm. Similar to the top graph, both CuO and  $\text{Cu}_2\text{O}$  features can be found in all the samples. The most significant change is that a peak



near  $\sim 300\text{ cm}^{-1}$  starts to appear at the highest temperatures. This new peak is also characteristic of CuO, particularly when it is located at the surface, as it has been frequently observed when original  $\text{Cu}_2\text{O}$  starts to transform into CuO. Hence, the appearance of this  $\sim 300\text{ cm}^{-1}$  peak indicates that the preferred  $\text{Cu}_2\text{O}$  phase is starting to be replaced by a CuO phase as the deposition temperature increases.

Following the characterization of the  $\text{CuO}_x\text{:N}$  films, their application to transport holes out of a crystalline silicon wafer, that is, to form simple hole contacts, was investigated. To evaluate such application, the contact resistivity,  $\rho_c$ , was measured by the Cox and Strack method using a point probe IV station.<sup>36</sup> To prepare the corresponding test structures, the  $\text{CuO}_x\text{:N}$  film was directly sputtered onto a p-type, (100) oriented,  $\sim 1.0\ \Omega\text{ cm}$  planar c-Si wafer, following which, a Pd(40 nm)/Ag(800 nm) metal stack was evaporated on top of it through a shadow mask, so that circular contacts with a range of different diameters were created. On the rear side of the wafer, a full-area Ohmic aluminium contact was applied, which makes a negligible contribution to the overall resistance. The measurement was performed. Figures 3(a)–3(c) present the contact resistivity results for  $\text{CuO}_x\text{:N}$  films deposited under various conditions. The contact resistivity results were extracted by modelling, using the resistance values calculated from I to V measurements for different dot sizes. Figure 3(d) shows representative I–V measurements of a particular film. A perfectly linear I–V behaviour was observed for all the samples presented in Figure 3, which confirms the formation of an Ohmic contact between the Ag/Pd/ $\text{CuO}_x\text{:N}$  stack and the silicon wafer. Such Ohmic behaviour is a consequence of the fact that both the silicon substrate and the  $\text{CuO}_x\text{:N}$  film are p-type. It is worth mentioning that  $\text{CuO}_x\text{:N}$  films deposited on n-type silicon wafers resulted in a rectifying contact. A similar rectifying behaviour has been observed between cupric oxide, CuO, and n-type silicon.<sup>37</sup> The implication is that, like CuO, the  $\text{CuO}_x\text{:N}$  films studied here can serve as a selective hole contact in silicon devices.

Figure 3(a) shows that  $\rho_c$  varies significantly with the oxygen flow rate during sputtering. This is primarily caused by the changing film composition, as identified by the XPS measurements described above. A moderate oxygen flow enables the formation of  $\text{Cu}_2\text{O}$  in the film and permits the incorporation of a small amount of N dopants, thus resulting

in a good conductivity. The contact resistivity presents at a minimum of  $\sim 11\text{ m}\Omega\text{ cm}^2$  for an  $\text{O}_2$  flow of 1.5 sccm. Poorer results are obtained when the  $\text{O}_2$  concentration is too low. This is likely related to the formation of  $\text{CuN}_x$  or copper precipitates, as discussed during XPS characterisation. On the other hand, an excess of oxygen leads to the preferential formation of CuO,<sup>15</sup> resulting in a higher contact resistivity.

The impact of sample temperature during film deposition on contact formation is shown in Figure 3(b), which shows that the optimal deposition temperature is  $100^\circ\text{C}$ . A temperature increase generally leads to a transition from  $\text{Cu}_2\text{O}$  to CuO,<sup>28</sup> which can explain the observed increase of  $\rho_c$  at temperatures above  $100^\circ\text{C}$ . Such phase transformation is shown by the Raman spectroscopy measurements in Figure 2. Nevertheless, the sample deposited at  $50^\circ\text{C}$  has a higher  $\rho_c$  than the sample deposited at  $100^\circ\text{C}$ . This is most likely caused by incomplete Cu– $\text{O}_2$  reaction. Similarly, an incomplete reaction may also occur for very short depositions, explaining the high  $\rho_c$  values measured for the thinner films shown in Figure 3(c). A similar thickness-dependent trend of  $\rho_c$  has also been seen for other conductive metal oxides.<sup>10</sup> A relatively thin film of about 8 nm is found to be optimal. Above that value, there is a significant increase of  $\rho_c$ . It should be noted that the deposition power, the chamber pressure, and the nitrogen flow rate can also have a significant impact on the contact formation. In this study, they were fixed at 60 W, 4 mTorr, and 5 sccm, respectively.

In conclusion, we have demonstrated that thin films of  $\text{CuO}_x\text{:N}$  deposited by reactive sputtering can form hole-selective contacts on p-type crystalline silicon, with a reasonably low resistivity  $\rho_c$  of  $\sim 11\text{ m}\Omega\text{ cm}^2$ . This result was achieved by optimising several process parameters, including the oxygen flow rate, the deposition temperature, and the film thickness. XPS measurements were used to determine the chemical composition of the films, revealing that the sputtered  $\text{CuO}_x\text{:N}$  is a mixture of cuprous oxide ( $\text{Cu}_2\text{O}$ ), cupric oxide (CuO) and, sometimes, a small amount of copper precipitates or  $\text{CuN}_x$ . The  $\text{CuO}_x\text{:N}$  films were also characterised by Raman spectroscopy, which further confirmed the existence of both  $\text{Cu}_2\text{O}$  and CuO phases. The Raman peaks provided evidence for the relationship between the oxygen flow and the formation of CuO or  $\text{Cu}_2\text{O}$  groups. They also revealed a transition from  $\text{Cu}_2\text{O}$  to CuO when the substrate temperature was increased. The low contact resistance achieved in this study

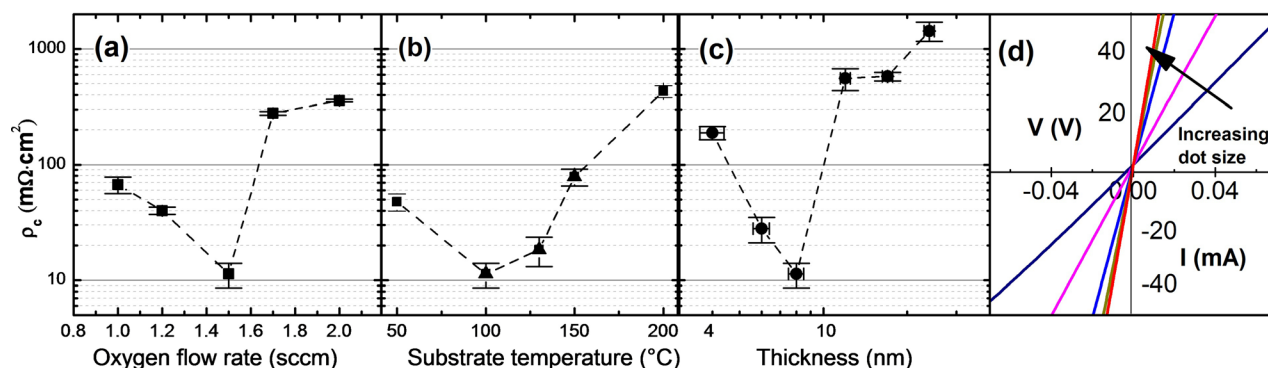


FIG. 3. Contact resistivity of a  $\text{CuO}_x\text{:N}/\text{Si}$  structure as a function of: (a) oxygen gas flow; (b) substrate temperature; (c)  $\text{CuO}_x\text{:N}$  films thickness; (d) example of the measured data.

shows that  $\text{CuO}_x\text{:N}$  films formed by sputtering deposition can play a significant role in the development of selective-contact structures for crystalline silicon solar cells.

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